

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
18 July 2002 (18.07.2002)

PCT

(10) International Publication Number
WO 02/055759 A2

(51) International Patent Classification⁷: C23F 11/00

(21) International Application Number: PCT/EP02/00522

(22) International Filing Date: 15 January 2002 (15.01.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/261,764	16 January 2001 (16.01.2001)	US
60/267,053	6 February 2001 (06.02.2001)	US
60/268,642	14 February 2001 (14.02.2001)	US

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN,
YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
NE, SN, TD, TG).

Published:

— without international search report and to be republished
upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: A CHEMICAL BASE FOR ENGINE COOLANT / ANTIFREEZE WITH IMPROVED THERMAL STABILITY PROPERTIES

(57) Abstract: An antifreeze/coolant for internal combustion engines which comprises: 1, 3-propanediol 97-98% by volume, 95 to 97 percent by weight; nitrite, 0.5 to 1.5%; nitrate, 0.30 to 1.5%; borate, 0.25 to 1.25%; mercaptobenzothiazole, 0.25 to 1.0%; tolyltriazole, 0.30 to 1.1%; benzyltriazole, 0.00 to 1.0%; silicate, 0.25 to 3.0%; antifoam, 0.05 to 0.3%; silicate stabilizer, 0.10 to 1.9%; and dye, 0.00 to 0.2%. An antifreeze/coolant for internal combustion engines which comprises: 1,3-propanediol 97/99% by volume, 95 to 97 percent; nitrite, 0.5 to 1.50% nitrate, 0.30 to 1.50%; phosphate, 0.50 to 1.60%; mercaptobenzothiazole, 0.25 to 1.00%, tolyltriazole, 0.30 to 1.10%; benzyltriazole, 0.00 to 1.00%; silicate, 0.25 to 3.00%; molybdate, 0.50 to 1.30% antifoam, 0.05 to 0.10%, and dye 0.00 to 0.02%. An antifreeze/coolant for internal combustion engines which comprises PDO 93 to 95% by weight, 2-ethylhexanoic acid 4.0 to 6.0%, sebacic acid 0 to 1.5%, sodium tolyltriazole 0.3 to 1.1%, antifoam 0.05 to 0.3% and dye 0 to 0.02%. An anti-freeze/coolant for internal combustion engines which comprises PDO 93 to 95% by weight, sodium nitrite 0.5 to 1.5%, 2-ethylhexanoic acid 4.0 to 6.0%, sebacic acid 0 to 1.5%, sodium tolyltriazole 0.3 to 1.0%, antifoam 0.05 to 0.3% and dye 0 to 0.02%. An antifreeze/coolant for fuel cell vehicles which comprises 1, 3 propanediol.

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A CHEMICAL BASE FOR ENGINE COOLANT / ANTIFREEZE WITH
IMPROVED THERMAL STABILITY PROPERTIES

Field of the Invention

The present invention relates to antifreeze/coolants which can be used for internal combustion engines and fuel cells. More particularly, the present invention
5 relates to such compositions which contain mostly 1,3-propanediol as the primary antifreeze/coolant and can also contain other ingredients as required for the particular use.

Background of the Invention

10 Increasingly challenging international engine emissions reductions have resulted in some advances in engine emissions technologies that may motivate a change from the customary ethylene glycol and/or propylene glycol bases that have been the mainstay of engine
15 antifreeze formulations for almost a century. The new engines' components, especially exhaust gas recirculation (EGR) devices, generate much greater thermal stress on the engine coolant. The oxidation of ethylene glycol and propylene glycol may be accelerated dramatically,
20 resulting in coolant unsuitable for continued use in as little as a few months. The industry has been working towards extended engine coolant service intervals, with some recommendations for service extended to as long as five years. It follows, therefore, that a requirement for
25 coolant change at four to six month intervals (due to accelerated oxidation and ageing) would be unacceptable to vehicle owners. There are other technologies than EGR for lowering exhaust emissions that have similar

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problems. The present invention is also advantageous for those other emissions lowering technologies.

Coolants are generally evaluated and judged by subjecting them to a series of physical properties and performance tests and then comparing the data to the specifications published by ASTM. The present invention relates to a new coolant base chemistry, known here as 1,3-propanediol by Shell, which is tested according to the ASTM D3306 Light and Medium Duty (Automotive) and D6210/6211 "Fully Formulated Engine Coolant" physical and performance testing protocols. These protocols qualify an engine coolant for use in virtually any engine cooling system, gasoline (petrol), diesel, and natural gas; engineered with or without wet sleeve cylinder liners.

Diesel engine original equipment manufacturers (OEMs) are vigorously working to prepare low-emissions diesel-fuelled engines that will meet the emissions requirements of North American and European regulatory agencies in the first decade of the twenty-first century. Extensive investments and research into various possible design improvements have generated some effective technologies such as exhaust gas recirculation devices (EGRs), referred to above. EGR devices, as the name implies, pass part of the exhaust gas back to the combustion chamber to increase the combustion efficiency of the engine, resulting in the lowering of target emissions. Exhaust gases, especially those produced by a diesel engine, are much hotter than regular intake air. The EGR gases, therefore, must be cooled by the existing engine coolant system before they reach the combustion chamber.

Coolant blended from ethylene glycol (EG) for heavy-duty diesel applications in prototype EGR-equipped

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engines sometimes experiences discolouration and rapid oxidation. Oxidation reactions include nitrite (NO_2) to nitrate (NO_3) and ethylene glycol ($\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$) to formic acid (CH_3-OOH) and glycolic acid ($\text{HO}-\text{CH}_2-\text{CH}_2-\text{OOH}$).

5 In the presence of the EGR, EG degradation is greatly accelerated. This degradation results in an increase in corrosive properties that attack engine components and cause premature failure. Although propylene glycol (PG) coolants have not been tested with EGR devices, PG is
10 generally considered even less thermally stable than EG.

The diesel engine emissions requirements for the model year 2002 heavy-duty diesel engines have resulted in experimentation with exhaust gas recirculation devices. Diesel engines with EGRs have been developed and
15 tested in various environments. In some tests the engine coolant turned black and produced a strong, unpleasant odour. Chemical analysis of the used coolant revealed very high concentrations of formates and glycolates. In addition, the nitrite concentration had been prematurely
20 depleted by oxidation to nitrate, as was the silicate. The coolants' pH had dropped from 10.2 to 8.3 in just a few months' service. Overall, this change results in a corrosive coolant that may attack, and cause premature failure of, cooling system components.

25 Ethylene glycol (1,2-ethanediol) and propylene glycol (1,2-propanediol) have offered the lowest-cost chemical bases for engine antifreezes/coolants for many decades. The current ASTM specifications for EG based engine coolants are ASTM D3306 (automotive and light
30 duty) and D6210 (fully formulated heavy duty). If EG and PG were found to be incapable of service in EGR-equipped

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diesel engines, 1,3-propanediol offers a more stable, longer lived alternative.

Summary of the Invention

The present invention relates to a antifreeze/
5 coolant composition for use in internal combustion engines which comprises: an anti freeze/coolant for internal combustion engines which comprises: 1,3-propanediol (PDO) 97-98% by volume, 95 to 97 percent by weight; nitrite, 0.50 to 1.5%; nitrate, 0.30 to 1.5%;
10 borate, 0.25 to 1.25%; mercaptobenzothiazole, 0.25 to 1.0%; tolyltriazole, 0.30 to 1.1%; benzyltriazole, 0.00 to 1.0%; silicate, 0.25 to 3.0%; antifoam, 0.05 to 0.3%; silicate stabilizer, 0.10 to 1.9%; and dye, 0.00 to 0.02%

In another embodiment, the present invention relates
15 to a different antifreeze/coolant composition for use in internal combustion engines which comprises: an anti freeze/coolant for internal combustion engines which comprises: 1,3-propanediol 97-98% by volume, 95 to 97 percent by weight; nitrite, 0.50 to 1.50%; nitrate, 0.30
20 to 1.50%; phosphate, 0.50 to 1.60%; mercaptobenzothiazole, 0.25 to 1.00%; tolyltriazole, 0.30 to 1.10%; benzyltriazole, 0.00 to 1.00%; silicate, 0.25 to 3.00%; molybdate, 0.50 to 1.30%; antifoam, 0.05 to 0.10%, and dye 0.00 to 0.02%.

In another embodiment, PDO is 93 to 95% by weight, 2-ethylhexanoic acid is 4.0 to 6.0 %, sebacic acid is 0
25 to 1.5%, sodium tolyltriazole is 0.3 to 1.1%, antifoam is 0.05 to 0.3% and dye is 0 to 0.02%. In a fourth embodiment, PDO is 93 to 95% by weight, sodium nitrite is
30 0.5 to 1.5%, 2-ethylhexanoic acid is 4.0 to 6.0 %, sebacic acid is 0 to 1.5%, sodium tolyltriazole is 0.3 to 1.1%, antifoam is 0.05 to 0.3% and dye is 0 to 0.02%.

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In still another embodiment, PDO is used as a coolant in fuel cell vehicles, i.e. there is provided an antifreeze/coolant for fuel cell vehicles which comprises 1,3-propanediol. It provides high electrical resistance, corrosion protection without traditional corrosion inhibitors, freeze protection to at least -44°C, improved operator safety by not conducting an intense electric field to serviceable components, and offers the optional embodiment of dilution up to 60 percent by weight with deionised water for improved economy.

In accordance with the present invention there is also provided a method for temperature protection of fuel cells used in fuel cell vehicles which comprises using 1,3-propanediol in the fuel cell as an antifreeze/coolant.

In accordance with the present invention there is further provided in a method for making an antifreeze/coolant composition for internal combustion and fuel cell engines comprising 1,3-propanediol 97-98% by volume, 95 to 97 percent by weight; nitrite, 0.50 to 1.50%; nitrate, 0.30 to 1.50%; phosphate, 0.50 to 1.60%; mercaptobenzothiazole, 0.25 to 1.00%; tolyltriazole, 0.30 to 1.10%; benzyltriazole, 0.00 to 1.00%; silicate, 0.25 to 3.00%; molybdate, 0.50 to 1.30%; antifoam, 0.05 to 0.10%, and dye 0.00 to 0.02%, which comprises first blending the nitrite, nitrate, phosphate, mercaptobenzothiazole, tolyl triazole, benzyl triazole, silicate, molybdate, antifoam, and optional dye in water and then adding 1,3-propanediol to the blend.

Brief Description of the Drawings

The present invention will now be described by way of example with reference to the accompanying drawings in which:

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Figure 1 illustrates the aqueous solution freeze point characteristics of the 1,3-propanediol and GM 6043 inhibition chemistry (EG).

Figure 2 shows the anions present in Type 'A' Coolants.

Figure 3 shows the anions present in Type 'B' Coolants.

Detailed Description of the Invention

1,3-propanediol, which is manufactured by Shell Chemical Company, is generally made as described in US-A-5304691 and the art described therein. This is a process for making PDO and HPA (3-hydroxypropanal, a 3-hydroxyaldehyde). In this particular patent, PDO and HPA are made by intimately contacting an oxirane (ethylene oxide, hereinafter 'EO'), a ditertiary phosphine-modified cobalt carbonyl catalyst, a ruthenium catalyst promoter, and syngas (carbon monoxide and hydrogen) in an inert reaction solvent at hydroformylation reaction conditions. A PDO yield of up to 86-87 mole% is reported, using a catalyst comprising cobalt ligated with 1,2-bis(9-phosphabicyclononyl)ethane as bidentate ligand, and either triruthenium(0) dodecarbonyl or bis[ruthenium tricarbonyl dichloride] as cocatalyst. Other methods of making PDO are known.

The present invention is a PDO-based antifreeze/coolant composition which is intended to be blended with water and used as the heat exchange medium in the cooling systems of internal combustion engines, especially diesel engines. It may also be used in cooling systems of other internal combustion engines. The PDO is the basic ingredient and it comprises from 95 to 97 percent by weight of the composition. However, the composition must also contain an inhibitor package. There are at least

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basically four types of inhibitor packages. One which contains a borate compound, Type A below, such as borax (sodium borate). Another type of inhibitor, Type B below, package instead contains a phosphate, such as sodium phosphate, and also a molybdate, such as sodium molybdate. Then there are the organic acid and heavy duty organic acid inhibitor packages. These are generally and specifically described in the following tables.

Table 1: TYPE 'A'

10

Chemical Percentage

1,3-Propanediol 97-98% by volume	95 to 97 percent
Sodium Nitrite	0.50 to 1.5 %
Sodium Nitrate	0.30 to 1.5 %
Borax	0.25 to 1.25 %
Sodium Mercaptobenzothiazole	0.25 to 1.0 %
Sodium Tolyltriazole	0.30 to 1.1%
Sodium Benzyltriazole	0.00 to 1.0%
Sodium Silicate	0.25 to 3.0%
Antifoam	0.05 to 0.3%
Silicate stabilizer	0.10 to 1.9%
Dye	0.00 to 0.02%

Table 2: TYPE 'B'

Chemical Percentage

1,3-Propanediol 97-98% by volume	95 to 97 percent
Sodium Nitrite	0.50 to 1.50 %
Sodium Nitrate	0.30 to 1.50 %
Sodium Phosphate	0.50 to 1.60 %
Sodium Mercaptobenzothiazole	0.25 to 1.00 %
Sodium Tolyltriazole	0.30 to 1.10%
Sodium Benzyltriazole	0.00 to 1.00%
Sodium Silicate	0.25 to 3.00%
Sodium Molybdate	0.50 to 1.30%
Antifoam	0.05 to 0.10%
Dye	0.00 to 0.02%

15

Both compositions contain from 0.5 to 1.5 weight percent of a nitrite, such as sodium nitrite, and from 0.3 to 1.5 weight percent of a nitrate, such as sodium

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nitrate. The nitrate ion provides protection from pitting and crevice corrosion.

Both compositions must contain from 0.25 to 3.0 weight percent of a silicate, such as sodium silicate. The
5 silicate may be present in any of its various forms. The purpose of a silicate is to offset the corrosion tendencies of the phosphate ion in one of the compositions and also to provide corrosion protection to aluminium heat rejecting surfaces, including engine heads and radiators.

10 Both compositions must contain the indicated amounts of mercaptobenzothiazole, tolyltriazole, and benzyltriazole. These azoles protect copper and copper alloys from corrosion by forming an impervious film with copper on the metal.

15 The borate containing composition must contain from 0.25 to 1.25 weight percent of the borate, such as borax. The borate may be present in any of its various forms. Borate is a good pH buffer. It is used to offset the tendency of the pH of the composition to decrease when
20 acidic exhaust gases from the engine get into the composition.

Any other composition, from 0.5 to 1.6 weight percent of phosphate, such as sodium phosphate, must be present. It is important in the protection of the metal
25 surfaces from cavitation corrosion and also provides corrosion protection to ferrous metal components.

It is desirable to include an effective amount of an antifoaming composition in the antifreeze/coolant composition. Such components are well known.

30 Polyglycol-type antifoaming agents can be used. In the borate composition, the amount of antifoam ranges from 0.05 to 0.3 weight percent and in the phosphate.

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composition, the antifoam may comprise 0.05 to 0.10 weight percent of the composition.

Table 3: Organic Acid

5	Chemical	Percentage
	1,3-Propanediol 97% to 98% by volume	93 to 95 percent
	2-Ethylhexanoic acid	4.0 to 6.0 %
	Sebacic acid	0.0 to 1.5 %
	Sodium Tolyltriazole	0.30 to 1.1%
	Antifoam	0.05 to 0.3%
	Dye	0.00 to 0.02%

Table 4: Heavy Duty Organic Acid

10	Chemical	Percentage
	1,3-Propanediol 97% to 98% by volume	93 to 95 percent
	Sodium Nitrite	0.50 to 1.50 %
	2-Ethylhexanoic acid	4.0 to 6.0 %
	Sebacic acid	0.0 to 1.5 %
	Sodium Tolyltriazole	0.30 to 1.10%
	Sodium Molybdate	0.50 to 1.30%
	Antifoam	0.05 to 0.10%
	Dye	0.00 to 0.02%

We have also found that organic acid inhibitor packages are effective in the PDO antifreeze/coolant compositions. The Organic Acid table above describes such a composition. The Heavy Duty Organic Acid table above describes another antifreeze/coolant composition containing PDO.

The use of PDO also allows formulation of antifreeze/coolants with environmentally friendly additives, perhaps eliminating the need for nitrite which is unacceptable for use in Europe.

It is believed that PDO coolants in fuel cell vehicles would have an electrical resistivity of greater than 250 kOhm-cm, a boiling point of greater than 90°C, a freezing

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point of less than -40°C, a thermal conductivity of greater than 0.4 W/m-k, a viscosity of less than 1 mPa.s (1 cPs) at 80°C and less than 6 mPa.s (6 cPs) at 0°C, a heat capacity of greater than 3 kJ/kg-K, a durability of greater than
5 5000 hours of operation (three years total time), material compatibility - will not corrode or erode current automotive cooling system materials, have a toxicity classified as non-toxic for transportation, and will be cost competitive with current automotive coolants.

10 The PDO formulations give intrinsically better protection against cavitation than EG or PG.

It is the theory that some or all of these advantages are based upon the relative chelation ability of PDO versus EO and PO. The latter are readily able to chelate the ions
15 in the solution. The chelate with EO and PO will be a five-membered ring which is relatively easy to form. PDO cannot chelate the ions in solution very well because it has to form a six-membered ring and this is very hard to do.

20 EXAMPLES

In order to learn if the new chemistry offered benefits compared to EG based engine coolants, three sets of ASTM D3306 / D6210 style test protocols were commissioned. These tests followed the ASTM protocol,
25 except that the testing temperatures were increased to the maximum safe operating temperature of each performance testing apparatus. This adaptation was designed to increase the severity of the test, to simulate the increased thermal stress contributed by the
30 EGR equipped diesel engines, and to learn if the new chemistry would resist premature ageing better than EG. Each test pair included an EG and a 1,3-propanediol fluid

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prepared per the appropriate ASTM standard test methods. Each of the three pairs represented one inhibitor chemistry.

Automotive (light duty)

5 The first round of tests evaluated 1,3-propanediol inhibited with an inhibitor package described in the GM 6043 antifreeze formulation/specification. This inhibitor package, in EG, represented the factory-fill for all North American GM cars until 1994. Its properties are
10 well known and the chemistry offered a good opportunity to assess the probable performance of 1,3-propanediol by using ASTM laboratory tests.

 Inhibited with the GM 6043 chemistry, the 1,3-propanediol performed somewhat better than EG in modified
15 ASTM-type tests. Figure 1 illustrates the aqueous solution freeze point characteristics of the 1,3-propanediol and GM 6043 (EG). There is a slight compromise of freeze protection as determined by the ASTM D1177 test method, but the 1,3-propanediol was soft and slushy at the
20 reported freeze point. This could be an indication that actual protection against hard, damaging freezing is actually better, approaching the effective protection point of the EG-based product. The D1177 test was also performed with 55% and 60% 1,3-propanediol in water, and
25 it was found that the 55% concentrated product offered protection equivalent to 50% EG, per the test method. Freeze protection continued to improve at 60% 1,3-propanediol. It is felt that the antifreeze properties of the chemistry are acceptable. Indeed a 50% solution would
30 provide adequate protection against freezing in most geographies.

 The boiling point of the 50% solution by ASTM D1120 is 106°C, one degree lower than the 50% EG at 107 °C.

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1,3-propanediol has a slightly lower Specific Gravity (SG) than EG when measured by the ASTM D1122 method. The EG based antifreeze was found to have a SG of 1.129 whereas the 1,3-propanediol SG was measured at 1.070.

5 Neither coolant had any effect when subjected to the Effect on Automotive Finish evaluation (ASTM D1882). Indeed, as illustrated below, many of the physical properties of the two coolants are very similar. The similarity is beneficial, because the new coolant will
10 almost certainly be contaminated from time to time with EG and/or PG based coolants. When contamination occurs, it would be desirable that no harm to the system result. Presumably only some of the anti-oxidation benefit would be lost.

15 The water content of the antifreeze is contributed by the inhibition technology, so there is no difference in the two base alternatives. Similarly, pH, chloride and ash characteristics were equivalent. The foaming tendency of the 1,3-propanediol was slightly higher, but remained
20 within the ASTM D3306 limits. (Tables 5, 6, and 7)

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Table 5: Physical Tests

Test Number & Description	1,3-propanediol 6043	GM 6043 (EG)
D1122 Specific Gravity	1.070	1.129
D1177 Freeze Point 50% vol. in water	-28 °C (-18 °F)	-38 °C (-36 °F)
D1120 Boiling Point 50% vol. in water	106 °C (222 °F)	107 °C (226 °F)
D1882 Auto Finish Effect	None	None
D1119 Ash Content	0.81 %	0.87%
D1287 pH: 50% vol. in DI water	9.8	8.67
D3634 Chloride	16	11
D1123 Water, mass percent	4.1%	4.0%
D1121 Reserve Alkalinity	9.8	9.3
D1881 Foaming Tendencies	Break 3.6 Sec Vol. 113 ml	Break 1.6 Sec Vol. 50 ml

Table 6: Glassware Tests

5

Test Number & Description	1,3-propanediol 6043	GM 6043 (EG)
D4340 Corrosion of Aluminium Heat Rejecting Surface	0.27 mg/cm ² /week	0.12 mg/cm ² /week
D1384 Corrosion in Glassware	Cu 3 mg Solder 1 mg Brass 2 mg Steel 1 mg Cast Fe 2 mg Cast Al 0 mg	3 mg 1 mg 2 mg 1 mg 1 mg 0 mg

Table 7: Performance Tests

Test Number & Description	1,3-propanediol 6043	GM 6043 (EG)
D2570 Simulated Service	Cu 3 mg Solder 0 mg Brass 7 mg Steel 1 mg Cast Fe 0 mg Cast Al 4 mg	5 mg 4 mg 0 mg 3 mg 3 mg 1 mg
D2809 Water Pump Cavitation-Erosion	8	8

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The data reported to this point were developed to learn if 1,3-propanediol had potential as an engine coolant. The data prove that the properties of the new chemistry are favourable, and justified further research.

5 The next stage of research targeted commercial fleet engines.

Fully Formulated (heavy duty)

The second round of tests evaluated 1,3-propanediol as a heavy-duty or 'universal' fleet-targeted coolant. This course of testing was undertaken because of reports that EG-based coolants in heavy duty diesel trucks equipped with prototype EGR devices were turning black and corrosive in less than three months / 50,000 km. To determine the viability of 1,3-propanediol as a heavy-duty coolant, it was prepared with both the ASTM D6210 type 'A' and type 'B' inhibitor chemistries. These chemistries, in addition to the requirements that they meet the performance specifications for cars and light trucks, are required to contain chemistry to protect wet sleeve liners against cavitation-erosion. The tests were run against an EG control. The coolant samples were all prepared in the laboratory, using the same inhibitor provided by two major inhibitor manufacturers.

25 Type 'A' and Type 'B' inhibitor packages are set out in Tables 1 and 2 above.

1,3-propanediol appears to offer intriguing advantages. The data, reported in Tables 8-10, reveal potential advantages in reduced oxidation (ageing) and advantages in corrosion protection, especially protection against lead solder bloom. These tests were run at higher temperatures, where possible, than is specified by ASTM D6210, so the data should not necessarily be viewed as

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'pass' or 'fail' per the standard, but as research experiments.

In the elevated temperature aluminium heat rejection test, D4340, reported in Table 9, the coolants were operated for 168 hours at 150 °C. The standard method specifies 168 hours at 135 °C. Similarly, the temperature was elevated in the D1384 and D 2570 to the maximum sustainable in the equipment. The operating temperature modifications are noted in the data tables, below:

10

Table 8: Physical Properties

Test Number & Description	1,3-propanediol 6210 'A'	Control EG 6210 'A'
D1122 Specific Gravity	1.067	1.127
D1177 Freeze Point 50% vol. in water	-30 °C (-21 °F)	-38 °C (-36 °F)
D1120 Boiling Point 50% vol. in water	107 °C (226 °F)	107 °C (226 °F)
D1882 Auto Finish Effect	No effect	No effect
D1119 Ash Content	0.55%	0.80%
D1287 pH: 50% vol. in DI water	11.25	11.0
D3634 Chloride	24	25
D1123 Water, mass percent	<3.0%	<3.0%
D1121 Reserve Alkalinity	6.8	8.8
D1881 Foaming Tendencies	Break 3.3 Sec Vol. 65 ml	Break 2.1 Sec Vol. 55 ml

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Table 9: Glassware Tests

Test Number & Description	1,3-propanediol 6210 'A'	Control EG 6210 'A'
D4340 Corrosion of Aluminium Heat Rejecting Surface @150 °C	0.28 mg/cm ² /week	0.20 mg/cm ² /week
pH Before & After Test	11.3 & 8.6	11.0 & 8.2
D1384 Corrosion in Glassware @ 150 °C	Cu 3 mg Solder 2 mg Brass 2 mg Steel 1 mg Cast Fe 0 mg Cast Al 4 mg	4 mg 26 mg 2 mg 1 mg 0 mg 0 mg

Table 10: Performance Tests

Test Number & Description	1,3-propanediol 6210 'A'	Control EG 6210 'A'
D2570 Simulated Service @ 87 °C	Cu 12 mg Solder 11 mg Brass 4 mg Steel 3 mg Cast Fe 0 mg Cast Al 0 mg	8 mg 56 mg 1 mg 1 mg 1 mg 0 mg
D2809 Water Pump Cavitation-Erosion	8	3

The data are interesting in that, in this set of tests, two of the annoying tendencies of "type A" formulations are soundly dampened by the 1,3-propanediol. Namely, the solder corrosion in D1384 and D2570 and the water pump erosion sometimes seen in the D2809, as was reported in this sequence. The coolant from the Simulated Service tests, which requires about ten weeks to complete, was analysed after the test to see if any resistance to oxidation could be documented.

This data suggested that high temperature characteristics of 1,3-propanediol may be better, that it

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may resist degradation compared to EG while offering equivalent to slightly better corrosion protection evidenced by D1384 and D2570 data. In particular, chemical analyses of the coolants was conducted to
5 quantify and compare the degradation of coolants as evidenced by the concentration of oxidation products. As coolant ages in use, some of the glycols oxidise. Ethylene Glycol may form formic acid ($\text{CH}_3\text{-COOH}$) or either of two C_2 molecules: glycolic acid ($\text{HO-CH}_2\text{-COOH}$) or
10 oxalic acid ($\text{HOOC-CH}_2\text{-CH}_2\text{-COOH}$). 1,3-propanediol was also reviewed for larger carboxylates, in case degradation of this chemistry might produce them (Figure 2).

1,3-propanediol inhibited with a "Fully Formulated Type 'A' Inhibitor Package" produced very positive data.
15 In the high temperature testing, data either were equivalent to or better than the EG. Significant improvements were documented in lead solder performance, aluminium water pump erosion/corrosion and degradation of the coolant chemical base.

20 Corrosion in Glassware, the ASTM D 1384 method, was performed with the standard set of six metal samples. The data for each the six metals are reported in table 9. The standard test requires 336 hours of exposure at 88 °C. This test was run for 336 hours at 150 °C by using a
25 propylene glycol bath instead of water. Similarly, The coolant temperature was elevated in the D4340 apparatus.

The maximum safe operating temperature of the simulated service rig was deemed to be 93 °C, five degrees warmer than the normal operating temperature of
30 88 °C. In general, the data from the simulated service paralleled that of the Corrosion in Glassware test.

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Finally, the two coolants were evaluated in the Hot Surface Scale test. There are currently no ASTM requirements or suggestions for limits in scale formation resulting from this method. The method involves

5 introducing a fluid consisting of 8 vol% of the sample mixed in corrosive hard water into the test apparatus. The apparatus is operated for 100 hours, exposing the sample to a hot steel surface in order to learn if the chemistry can prevent the formation of scale. The control

10 'type A' performed somewhat better than the new 'type A', but both performed well. The control generated 1.6 milligrams of scale and the new chemistry 2.3 milligrams. Uninhibited ethylene glycol and hard water typically accumulate about 5 milligrams. This data suggests both

15 chemistries would prevent serious scale formation in service, a prediction that has been confirmed by positive fleet experience with the 'type A' formulation in an ethylene glycol based coolant.

The research next turned to repeating the testing

20 using "Fully Formulated Type 'B' Inhibitor". The new chemistry surprised the researchers by displaying unexpected reactions in the course of blending the 'type B' formulation-it solidified. Although a most intriguing event, this behaviour was not useful in the evaluation of

25 the product as an engine coolant. Experimentation finally succeeded in a method that required first blending the 'type B' inhibitors in water and lastly adding the antifreeze chemistry to successfully produce the prototype product. If marketed, this variation may only

30 be available as a "ready-to-use" coolant. Of course, further formulation may find a way to overcome this most peculiar property.

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The 'type B' chemistry differs from the 'type A' in that it includes phosphate in place of borate and adds molybdate and an additional anti-cavitation inhibitor for wet-sleeve lined diesel engines. The two types of heavy-duty coolants herein evaluated are approximately equally represented in North American fleets. Type 'B' may be more a bit more common in the global marketplace. Chances are that the final formulations for both variations will be optimised for 1,3-propanediol. Each of the two has produced interesting data, each had advantages and disadvantages over the other.

Table 11: Physical Properties for Type 'B'

Test Number & Description	1,3-propanediol 6210 'B'	Control EG 6210 'B'
D1122 Specific Gravity	1.062	1.135
D1177 Freeze Point 50% vol. in water	-30 °C (-21 °F)	-38 °C (-36 °F)
D1120 Boiling Point 50% vol. in water	107 °C (226 °F)	108 °C (228 °F)
D1882 Auto Finish Effect	No effect	No effect
D1119 Ash Content	1.58%	1.76%
D1287 pH: 50% vol. in DI Water	10.6	10.5
D3634 Chloride	10	10
D1123 Water, mass percent	<3.0%	<3.0%
D1121 Reserve Alkalinity @ 50%	11.4	10.8
D1881 Foaming Tendencies	Break 4.2 Sec Vol. 215 ml	Break 2.2 Sec Vol. 85 ml

Table 12: Glassware Tests for Type 'B'

Test Number & Description	1,3-propanediol 6210 'B'	Control EG 6210 'B'
D4340 Corrosion of Aluminium Heat Rejecting Surface @150 °C	0.32 mg/cm ² /week	9.0 mg/cm ² /week
pH Before & After Test	8.3 & 8.3	8.9 & 10.0
D1384 Corrosion in Glassware @ 150 °C	Cu 2 mg Solder 2 mg Brass 1 mg Steel 2 mg Cast Fe 0 mg Cast Al 0 mg	1 mg 2 mg 2 mg 5 mg 7 mg 0 mg

Table 13: Performance Tests for Type 'B'

Test Number & Description	1,3-propanediol 6210 'B'	Control EG 6210 'B'
D2570 Simulated Service @ 87 °C	Cu 3 mg Solder 1 mg Brass 8 mg Steel 2 mg Cast Fe 0 mg Cast Al 1 mg	1 mg 58 mg 1 mg 0 mg 0 mg 8 mg
D2809 Water Pump Cavitation-Erosion	9	8

In 1,3-propanediol, an optimised chemistry offers an excellent performing product that offers long service intervals and superior corrosion protection. The data for the Type 'B' formulation is set out above in tables 11, 12 and 13.

The hot scale test was also performed on the 1,3-propanediol type "B". There was no scale formed on the hot surface (0.0 mg). The test stand was inspected, and the correctness of the test has been verified. The EG control experiment generated 1.75 mg of scale.

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The data from the type 'B' experiments are similar to the data from the type 'A'. There is evidence that the oxidation of the coolant is faster in EG than in 1,3-propanediol. This evidence is that the formates and glycolates are significantly lower in 1,3-propanediol than in EG-based coolant. The same may be observed in the sulphate, usually present as an oxidation product of mercaptobenzothiazole (MBT). Interestingly, the nitrite concentration was lower in both type 'A' and type 'B' coolants in 1,3-propanediol.

A prospective new base chemical has been discovered that resists oxidation due to thermal stress better than ethylene glycol. The chemistry, 1,3-propanediol, may be successfully inhibited with conventional light duty and fully formulated engine coolant inhibition technologies. The coolant base has passed all of the standard ASTM tests at increased temperatures, demonstrating its capabilities in severe operation environments.

The chemistry described and claimed herein meets ASTM engine coolant performance standards.

C L A I M S

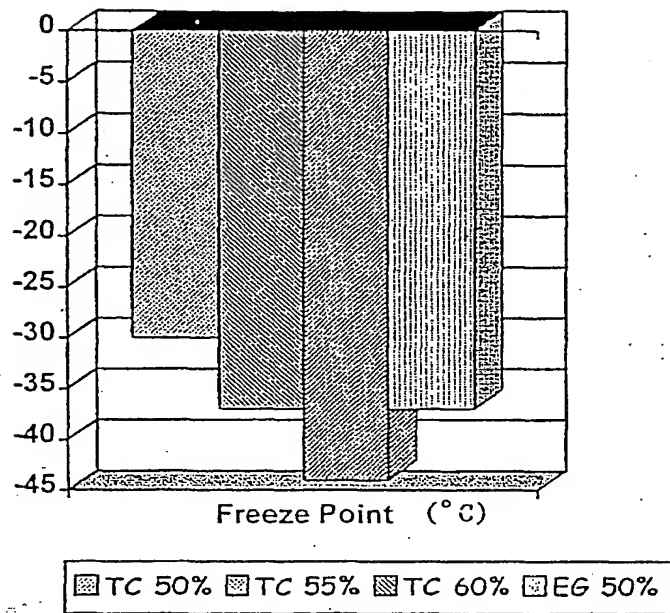
1. An antifreeze/coolant for internal combustion engines which comprises: 1,3-propanediol 97-98% by volume, 95 to 97 percent by weight; nitrite, 0.50 to 1.5%; nitrate, 0.30 to 1.5%; borate, 0.25 to 1.25%;
5 mercaptobenzothiazole, 0.25 to 1.0%; tolyltriazole, 0.30 to 1.1%; benzyltriazole, 0.00 to 1.0%; silicate, 0.25 to 3.0%; antifoam, 0.05 to 0.3%; silicate stabilizer, 0.10 to 1.9%; and dye, 0.00 to 0.02%
2. An antifreeze/coolant for internal combustion
10 engines which comprises: 1,3-propanediol 97-98% by volume, 95 to 97 percent by weight; nitrite, 0.50 to 1.50%; nitrate, 0.30 to 1.50%; phosphate, 0.50 to 1.60%; mercaptobenzothiazole, 0.25 to 1.00%; tolyltriazole, 0.30 to 1.10%; benzyltriazole, 0.00 to 1.00%; silicate, 0.25
15 to 3.00%; molybdate, 0.50 to 1.30%; antifoam, 0.05 to 0.10%, and dye 0.00 to 0.02%.
3. An antifreeze/coolant for internal combustion engines which comprises: 1,3-propanediol 93 to 95% by weight, 2-ethylhexanoic acid 4.0 to 6.0 %, sebacic acid 0
20 to 1.5%, sodium tolyltriazole 0.3 to 1.1%, antifoam 0.05 to 0.3% and dye 0 to 0.02%.
4. An antifreeze/coolant for internal combustion engines which comprises: 1,3-propanediol 93 to 95% by weight, sodium nitrite 0.5 to 1.5%, 2-ethylhexanoic acid
25 4.0 to 6.0 %, sebacic acid 0 to 1.5%, sodium tolyltriazole 0.3 to 1.1%, antifoam 0.05 to 0.3% and dye 0 to 0.02%.
5. An antifreeze/coolant for fuel cell vehicles which comprises 1,3-propanediol.

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6. A method for temperature protection of fuel cells used in fuel cell vehicles which comprises using 1,3-propanediol in the fuel cell as an antifreeze/coolant.

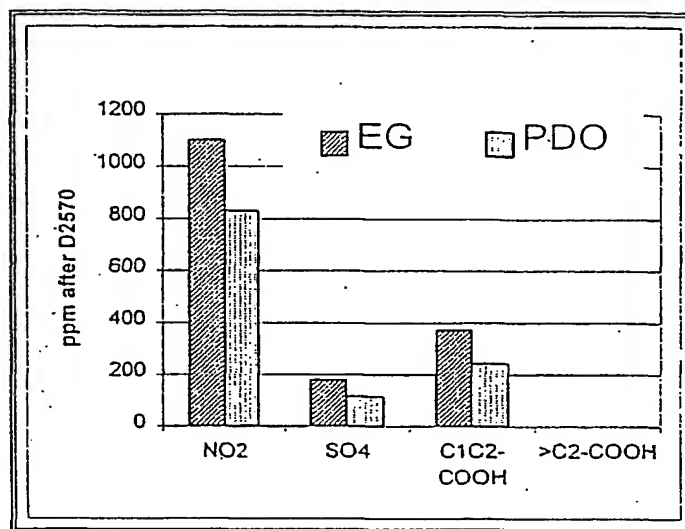
7. A method for making an antifreeze/coolant
5 composition for internal combustion and fuel cell engines comprising 1,3-propanediol 97-98% by volume, 95 to 97 percent by weight; nitrite, 0.50 to 1.50%; nitrate, 0.30 to 1.50%; phosphate, 0.50 to 1.60%;
mercaptobenzothiazole, 0.25 to 1.00%; tolyltriazole, 0.30
10 to 1.10%; benzyltriazole, 0.00 to 1.00%; silicate, 0.25 to 3.00%; molybdate, 0.50 to 1.30%; antifoam, 0.05 to 0.10%, and dye 0.00 to 0.02%, which comprises first
blending the nitrite, nitrate, phosphate,
mercaptobenzothiazole, tolyl triazole, benzyl triazole,
15 silicate, molybdate, antifoam, and optional dye in water and then adding 1,3-propanediol to the blend.

Figure 1



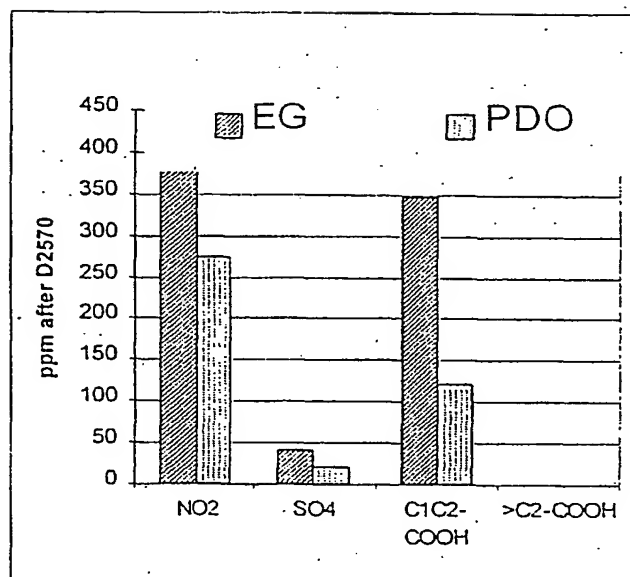
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Figure 2



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Figure 3



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(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
18 July 2002 (18.07.2002)

PCT

(10) International Publication Number
WO 02/055759 A3

(51) International Patent Classification⁷: **C09K 5/10**,
5/20, C23F 11/00, H01M 8/04

(21) International Application Number: PCT/EP02/00522

(22) International Filing Date: 15 January 2002 (15.01.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/261,764 16 January 2001 (16.01.2001) US
60/267,053 6 February 2001 (06.02.2001) US
60/268,642 14 February 2001 (14.02.2001) US

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,

CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN,
YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

(88) Date of publication of the international search report:
26 September 2002

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: A CHEMICAL BASE FOR ENGINE COOLANT / ANTIFREEZE WITH IMPROVED THERMAL STABILITY PROPERTIES

(57) Abstract: An antifreeze/coolant for internal combustion engines which comprises: 1, 3-propanediol 97-98% by volume, 95 to 97 percent by weight; nitrite, 0.5 to 1.5%; nitrate, 0.30 to 1.5%; borate, 0.25 to 1.25%; mercaptobenzothiazole, 0.25 to 1.0%; tolyltriazole, 0.30 to 1.1%; benzyltriazole, 0.00 to 1.0%; silicate, 0.25 to 3.0%; antifoam, 0.05 to 0.3%; silicate stabilizer, 0.10 to 1.9%; and dye, 0.00 to 0.2%. An antifreeze/coolant for internal combustion engines which comprises: 1,3-propanediol 97/99% by volume, 95 to 97 percent; nitrite, 0.5 to 1.50% nitrate, 0.30 to 1.50%; phosphate, 0.50 to 1.60%; mercaptobenzothiazole, 0.25 to 1.00%, tolyltriazole, 0.30 to 1.10%; benzyltriazole, 0.00 to 1.00%; silicate, 0.25 to 3.00%; molybdate, 0.50 to 1.30% antifoam, 0.05 to 0.10%, and dye 0.00 to 0.02%. An antifreeze/coolant for internal combustion engines which comprises PDO 93 to 95% by weight, 2-ethylhexanoic acid 4.0 to 6.0%, sebacic acid 0 to 1.5%, sodium tolyltriazole 0.3 to 1.1%, antifoam 0.05 to 0.3% and dye 0 to 0.02%. An anti-freeze/coolant for internal combustion engines which comprises PDO 93 to 95% by weight, sodium nitrite 0.5 to 1.5%, 2-ethylhexanoic acid 4.0 to 6.0%, sebacic acid 0 to 1.5%, sodium tolyltriazole 0.3 to 1.0%, antifoam 0.05 to 0.3% and dye 0 to 0.02%. An antifreeze/coolant for fuel cell vehicles which comprises 1, 3 propanediol.

WO 02/055759 A3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/00522

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09K5/10 C09K5/20 C23F11/00 H01M8/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K C23F H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EATON E R ET AL: "A CHEMICAL BASE FOR ENGINE COOLANT / ANTIFREEZE WITH IMPROVED THERMAL STABILITY PROPERTIES" SAE SPECIAL PUBLICATIONS, XX, XX, 2001, pages 55-61, XP008003886 ISSN: 0099-5908 the whole document	1-7
A	US 5 772 912 A (ZUK JOHN ET AL) 30 June 1998 (1998-06-30) column 19, line 16 - line 18 claims	1

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Date of the actual completion of the international search

24 July 2002

Date of mailing of the international search report

01/08/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

EP 02/00522

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5772912	A	30-06-1998	AU 717151 B2	16-03-2000
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